Novel Semi-Rigid Capsule Insulation Demonstration

Cooperative Research and Development Final Report

CRADA Number: CRD-18-00769

NREL Technical Contacts: Chaiwat Engtrakul and Lin Simpson

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Technical Report
NREL/TP-5900-79926
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Cooperative Research and Development Final Report

Report Date: May 4, 2021

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the final CRADA report, including a list of subject inventions, to be forwarded to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: FedIMPACT, LLC - affiliated with IP Group, Inc. (IPG)

CRADA Number: CRD-18-00769

CRADA Title: Novel Semi-Rigid Capsule Insulation Demonstration

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Sponsoring DOE Program Office:

Office of Energy Efficiency and Renewable Energy (EERE), Bioenergy Technologies Office (BETO)

Joint Work Statement Funding Table Showing DOE Commitment:

No NREL Shared Resources

Estimated Costs	NREL Shared Resources a/k/a Government In-Kind
Year 1	$.00
TOTALS	$.00

Executive Summary of CRADA Work:

This effort probed the novel use of capsule insulation to form an effective "solid" (as compared to powder) insulating "blanket," "panel," or other useful structures and to demonstrate important technical achievements, including crosslinking, thermal conductivity measurements, and achieving appropriate thermal and other properties needed to form high quality insulation that can directly and cost effectively address such markets as cryogenics and highly insulating panels.

Summary of Research Results:

Development of novel, highly insulating materials is needed to reduce U.S. energy consumption in nearly every economic sector, and thus will create U.S. jobs in nearly every economic sector from installation of such materials in buildings, vehicles, appliances, cryogenic equipment, and industrial processes. As DOE has correctly pointed out, even today with all the different insulation technologies available, revolutionary developments in insulation are needed and could reduce our energy use by several quads.[1] Imagine the U.S. manufacturing jobs and, ultimately, reduction of energy for heating and air conditioning that could be accomplished with a thin, inexpensive, and flexible highly-insulating material that contains only 5% to 15% air with no external encapsulant, and yet has such a flexible form factor that it is applicable to all kinds of applications. Present commercial insulation is typically limited by the thermal conductivity (TC) of air that in general fills most of the volume. Vacuum insulated panels (VIP) may surpass the air TC limit if a sufficient vacuum (~10^{-6} torr) can be held indefinitely. However, the VIP vacuum degrades relatively quickly (within a few years), is easily punctured, and VIPs are expensive, rigid, and must be pre-assembled to specific sizes/shapes. Thus, while VIPs have the potential to save quads of energy, their present DOE "SCOUT" estimates[1] indicate that VIPs will only address a small fraction due to their high cost and installation challenges. Therefore, there is a substantial need to develop a low cost, high R-value insulation with "flexible" form factors for diverse applications.

Our approach is to address the critical processes that are key to forming thin microcapsule insulation (MCI) with very high R-values (greater than R20/inch) to revolutionize different industries. The ultimate vision is to develop MCI that will cost effectively address many of the highest energy efficiency priorities DOE has identified to ultimately save quads of energy across just about all industrial sectors. Our nearer term goal with this project was to develop materials integration processes that enable us to demonstrate a strong, well-integrated insulation "panel" or "blanket" using microcapsules. This effort probed the novel use of evacuated microcapsules to form an effective "solid" (as compared to powder) insulating "blanket," "panel," or other useful form factors (Figure 1). The key to this technology was developing scalable and inexpensive novel processes and using inexpensive materials. This effort demonstrated important technical and business related achievements including:

1. Identified low-cost processes using commercially available materials to provide the appropriate crosslinking of the microcapsules to form useful, strong insulating structures while maintaining very low thermal conductivity. This included processes that can be performed at atmospheric pressures to eliminate the need for more expensive evacuated

[1] e.g., (a) https://www.energy.gov/sites/prod/files/2014/02/f8/BTO_windows_and_envelope_report_3.pdf, (b) http://aceee.org/files/proceedings/2016/data/papers/4_800.pdf

processing chambers. We also demonstrated potential inexpensive methodologies to adjust the strength, hydrophobicity, vapor transport, flexibility, and durability of the resultant microcapsule insulation (MCI) based on the application requirements.
2. Identified and demonstrated viable routes to increase the evacuated volume in the insulation, which will be critical to the final insulation value achieved.
3. Developed an initial technoeconomic analysis (TEA) model that indicates the MCI can be manufactured in large scale for less than $0.05/R/in-sf. This value is comparable to fiberglass batt insulation but with greater than R20/in (fiberglass batt insulation is R3/in).
4. Established the appropriateness for different measurement capabilities for our unique insulation samples. This included using a double shear test to quantify crosslinking strength, pycnometry to measure air space outside of microcapsules (packing density), measuring water vapor transmittance rates, and a novel thermal conductivity measurement protocol to accurately measure the absolute apparent/effective thermal conductivity (ATC). The ATC measurement is absolutely critical for future development and optimization of highly insulating materials because to date, no measurement system can provide absolute and accurate measurements on small "laboratory" scale samples with thermal conductivities less than 0.01 W/m-K at atmospheric pressure. This is important because our novel MCI samples will have ATCs between 0.001 W/m-K and 0.01 W/m-K, and rapid development and commercialization demands quick and accurate measurements of smaller samples to help select materials and optimize process parameters.
5. Fabricated novel MCI samples with measured TC values less than 0.01 W/m-K (experimental error +/- 0.005 W/m-K).

The detailed work for this short "demonstration" project is provided below and focuses on the crosslinking, TC measurements, and achieving appropriate thermal and other properties needed to form high quality insulation that can directly and cost effectively address high value markets.

Commercial/Business Development and Technical Task Outcomes:

Task 1: Project Management (Subtask 1.1 Project Management). This was a successful project with all project deliverables being provided on time and within budget with a summary technical report completed for the partner, unpublished yet summarized in this final report.

Task 2: Commercial/Business Development (Subtask 2.1. Technoeconomic Analysis and Market Identification). Today's super insulation is typically made from fumed silica that requires energy intensive high temperature flame processing or from aerogels that require expensive precursors and energy intensive and time consuming critical-point drying. These insulators are expensive, from $5 to $60 per square foot for R20, and only provide their best insulating properties when held in secondary containment systems under high vacuum, which has virtually no conductive or convective thermal transport. Maintaining the lightweight and reduction of thermal shorting provided by vacuum containing insulating systems is difficult. The vacuum in applications like VIP typically degrades within a few years and thus the insulation value decreases as well.

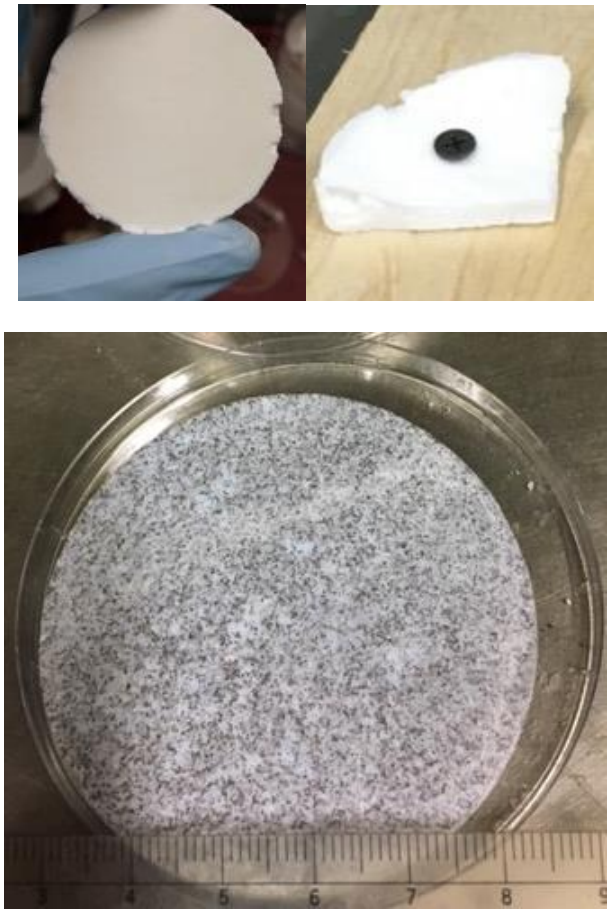

Figure 1. Solid insulative materials (top left) that can be attached to a piece of wood with a screw (top, right). NREL's crosslinked nanoporous lightweight (< 0.1g/cc) solid disk superinsulation with ~30% of the volume being vacuum held in vacuum capsules and ATC < 0.01 W/m-K (bottom).

Our microcapsules are powders that have thermal conductivities between 0.04 and 0.15 W/m-K. Microcapsules can be used to decrease thermal conductivity in host materials and can provide insulating properties because the gas/air inside typically has low thermal conductivity and if their wall thicknesses are relatively thin the overall apparent/effective thermal conduction is low. The ATC of materials with embedded microcapsules is dominated by the thermal conductivity of the host materials (e.g., polymers or ceramics), resulting in typical ATCs in the 0.1 to 1 W/m-K range. It is critical to develop packing and cross-linking methods to create products that can be easily integrated into various insulation markets while creating and maintaining low thermal conductivity properties of the microcapsules. NREL proposed and developed novel processing routes to insulative materials with low thermal conductivity (< 0.01 W/m-K).[2] Cross-linking of loose, insulating, evacuated microcapsules, capsules and/or particle powders results in inexpensive (as low as $0.05/R/in-sf) solid and potentially flexible insulating structures that can be handled and treated in a manner similar to many commercially available rigid foam panel insulations. The resulting solid insulative materials may be made by using standard manufacturing approaches such as roll-to-roll and continuous assembly processing at atmospheric or near atmospheric conditions to maintain low processing costs. In collaboration

2 "Crosslinking of Loose Insulating Powders." U.S. Provisional Patent Application No. 63/021,381.

with FedImpact/IP Group and Temple's Fox Business School, relevant market opportunities for MCI were identified. Of these applications identified, cryogenics and highly insulating panels were selected as the most attractive markets for MCI.

Task 3: Technical (Subtasks 3.1, 3.2, and 3.3. Strategies for Improving the Thermal and Mechanical Properties of Microcapsule Insulation – Packing, Cross-Linking, and Additives). Powdered microcapsules with no host matrix can be used as insulation, but their highly dispersible nature makes them difficult to work with and they are mostly only useful in mechanically strong structures that reduce the insulating value of the microcapsules, similar to the reduction of the insulative value of the microcapsules caused by being embedded in a polymer matrix. However, as with standard fiberglass insulation, air on the outside of the microcapsules is a better insulation than any solid matrix material, because the thermal conduction of air is only around 0.025 W/m-K and in the small spaces between the microcapsules there is virtually no convective heat transport.

To overcome the problems of creating insulative materials using microcapsules, the "dispersion issue" of dispersive particles can be resolved because the particles can be glued or bonded together in a number of different ways, without substantively increasing the effective thermal conductivity. For example, ceramic particles can be sintered at high temperatures to form a solid. However, this is energy intensive and significantly increases the thermal conductivity between particles as the sintered contact areas are substantially larger than the relatively small point contact areas between loose particles. Solution based processing has been used to glue/bond particles together. These processing methods have substantial issues associated with controlling surface wetting at the desired locations and removing the solvents without creating large air cavities in the structures that decrease the strength and potentially increases the thermal conductivity.

NREL successfully developed processing methods for making solid insulative materials comprised of crosslinked microcapsules. These solid insulative materials are capable of being nailed, screwed, cut and adhered to boards and papers without losing their structural integrity or substantially effecting the superior insulative properties of the material (Figure 1). Briefly, the evacuated microcapsules were crosslinked while maintaining optimal configurations enabling the intrinsic shape and structure to be designed and created. Either before or during the crosslinking processing step other processes can be used to increase the strength of the crosslinking bonds between the microcapsules or strengthen the insulative material composite. In both cases, the mechanical properties of the solid insulative material were improved (e.g., compression strength increased) while maintaining thermal conductivities less than 0.025 W/m-K. An open pore structure can be maintained in the solid MCI sample if desired to enable water vapor transport and minimize water condensation build up for some building applications. The MCI is inherently hydrophobic and does not allow liquid water to pass through as shown in Figure 2. To further decrease the thermal conductivity, solid insulative microcapsules were combined with opacifiers to decrease radiative transport and emissivity. Opacifiers were demonstrated that can be mixed with the microcapsules or integrated with subsequent processing.

Figure 2. Picture of hydrophobic MCI with a water drop beading up on the surface of the porous solid material.

Task 3: Additional work added in Mod 4 (Subtask 3.2. Validate Insulation Properties – Thermal Conductivity Measurement Protocols). Because of the myriad of thermal leaks from outside environmental components, obtaining accurate thermal conductivity measurements on the smaller samples often produced in R&D laboratories is very challenging. After years of investigating different measurement systems, NREL procured a unique thermal conductivity measurement system. This system to date is the only technique demonstrated to be able to provide "absolute" measurements of relatively small samples (i.e., 8" diameter by 1" thick or smaller) with thermal conductivities lower than 0.0001 W/m-K. However, most of the experience with this TC measurement system was under some amount of vacuum (especially for materials with thermal conductivities below 0.01 W/m-K), and therefore it was essential for NREL to develop procedures that provide reproducible measurements of highly insulating materials (i.e., below 0.01 W/m-K) at atmospheric pressures. NREL successfully performed systematic tests (Table 1) to identify "standard measurement protocols" that provided reproducible results enabling us to quantify the accuracy of the TC system for materials with thermal conductivities below 0.01 W/m-K at standard atmospheric pressures. To our knowledge this has not been accomplished previously, because until now there has not been materials with less than 0.01 W/m-K thermal conductivities in air. Several key factors were identified that may influence the TC measurements. These factors include:

1. Sample integration into the holder
2. Humidity and oxygen within the chamber and in the ambient air
3. Fill dynamics of the cold head
4. System equilibration time of the cold head
5. Inert gas purging of the chamber before and during measurements

Utilizing a standard insulating sample and performing repeated measurements, it was evident that active nitrogen purging of the chamber during measurements (to help control water vapor condensation on the cold head) induced substantial measurement variability within a run, run to run, and day to day. Interestingly, turning on the gas purge initially increased the thermal

conductivity measurement values (as expected due to increasing the amount of heat in the system), while turning off the gas purge decreased the measurement values. The overall impact of having active gas purging reduced the overall thermal conductivity measurement values. In general, the measurement process used is an intrinsically "chaotic" process that results in constant small fluctuations in the measurement. In addition, the system uses what has been described by the inventors as a "dynamic" approach such that the procedures that are used to fill the cold head and start the measurements may impact the measurements. These measurements fluctuations are exacerbated when operating at atmospheric pressures where the measurement times between coolant refills become very short due to the thermal conduction of air in the chamber resulting in more heating of the "guard" chamber. The end result of our initial studies is that thermal conductivity measurements may take several days to perform in order for the system to reach thermal equilibrium.

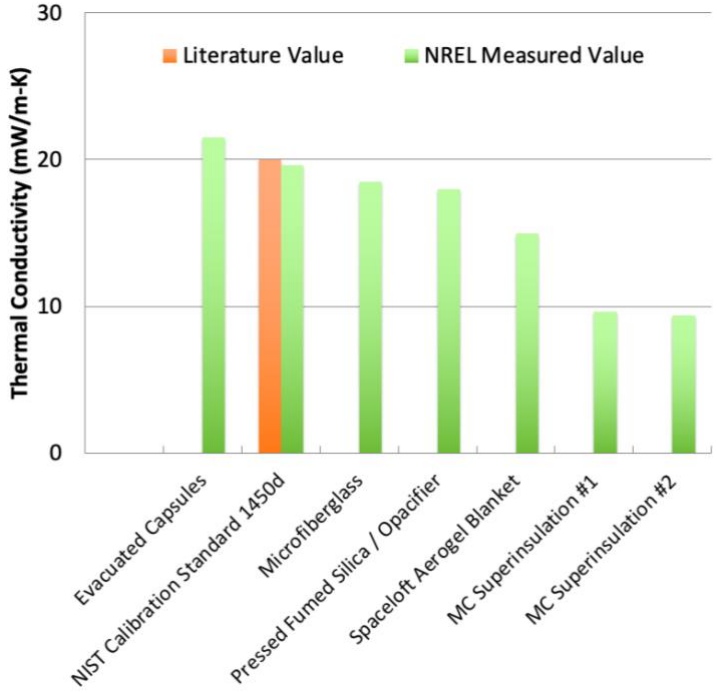

Figure 3. Plot comparing the measured apparent/effective thermal conductivities of different insulative materials, including the novel MCI samples.

A summary of the thermal conductivity measurement system procedure for achieving repeatable test conditions (at atmospheric pressure) includes the following:

1. The amount of water vapor inside the chamber must be controlled and minimized to reduce measurement variability. The change in relative humidity of the ambient air in the laboratory significantly impacts the measurement when the chamber is open to laboratory air. Active purging of the chamber with ultra-dry nitrogen/air alone is not adequate. Thus, the first step after the sample is loaded into the chamber is to evacuate the sample chamber if the sample will permit. Otherwise, purging the chamber with ultra-dry nitrogen/air until a dew point of less than -50 °C is achieved in the chamber is recommended. It may take 10 to 40 h of active evacuation of the chamber by a vacuum pump to remove the water adsorbed in the chamber.

2. Back fill the chamber with ultra-dry nitrogen/air to ~760 torr while keeping the chamber sealed from outside air.
3. Begin the measurement by following the standard protocol and adding coolant to the test and guard chambers.
4. Once completely filled with coolant, let the system rest for ~1 h to come to thermal equilibrium.
    a. A ~1 h wait time appeared to be sufficient, but longer wait times may be needed if the chamber is substantially out of thermal equilibrium (e.g., if heat is used to help degas the chamber additional time may be needed for the chamber to reach thermal equilibrium).
5. Refill the guard and test chambers with coolant and wait for ~15 minutes. Longer times did not seem to impact the measurement.
    a. Often the chamber may take 2 to 20 h to reach a final thermal equilibrium. At this point, the measured value of the test chamber must reach a constant value. This is the best measure for determining when the chamber has reached a thermal equilibrium.
6. The guard chamber will often run short of coolant long before the test ends. Under these conditions, refill just the guard chamber. This has the least amount of impact on the measurement.
7. While it may be possible to fill both the guard and test chambers if the temperature has risen substantially after an overnight period, it is recommended to restart the measurement by allowing the system to warm up to ambient temperature and beginning the procedure at step #1.

The procedure above reduced the measurement variability by well over 50% and enabled reproducible measurements. Figure 3 compares the measured ATCs of different insulative materials, including the novel MCI samples. Excellent agreement between literature and measured thermal conductivity values was obtained for a NIST calibration standard. Most importantly, the thermal conductivity values for two novel MCI samples were below 10 mW/m-K. A value of 9 mW/m-K (± 5) was measured for both MCI samples. Various control samples, including an evacuated capsules and pressed fumed silica with an opacifier, validated the superinsulation properties of the MCI samples. In both cases, the thermal conductivities of both control samples were well-above 10 mW/m-K (Figure 3). Additional work is needed to further reduce the measurement variability. For example, issues with sample loading into the chamber and extending measurement times may need to be resolved.

Table 1. Thermal Conductivity Measurement Qualification Test Parameters Evaluated.

Control Variables	Outcomes
Equilibration time after initial coolant fill	The following procedure appears to be appropriate: A 1 h wait time after the initial coolant fill, followed immediately by another fill and a 15 minute wait time. Exception, if the chamber is substantially hotter or colder than ambient prior to the initial coolant fill.
Number of coolant fills with hold times	Due to issues discussed below, most measurements will need to be performed with the first test fill and at most a second guard fill. A subsequent fill of both chambers is useful to see if there is repeatability but if there is a substantial change then the measurement needs to be restarted from the beginning.
Total time at cold source working temp	Depending on the sample, the chamber/test takes 4 to 12+ h to reach equilibrium after coolant is introduced. This may be longer if chamber is at sub-ambient pressures.
Hold time after top off	15 minutes appears to work well.
Refilling only guard	This is the preferred method to get reproducible data over a longer time period.
Amount of aerogel powder	Increasing the amount of aerogel powder to completely cover the top of the guard chamber appeared to improve reproducibility. Recommend 12-14 cups of aerogel fill or add until ~2” on top of guard.
Dew point of chamber after evacuation	In general, the dew point decreases once coolant is added because the guard chamber acts as a cold-mass vacuum pump.
Dew point in chamber/length of time evacuating	A low amount of water in the test chamber is critical for measurement reproducibility. Because of the high surface area of the aerogel insulation and perhaps of the sample, even opening the chamber in dry air conditions results in a lot of adsorbed water. Using a mechanical pump, it can take 10 to 30 h to reach a vacuum level of ~50 millitorr. This is one indicator that a substantial amount of water has been removed. However, this is not a sufficient indicator.
Monitor RH outside chamber	Outside RH does not impact the measurement if the chamber is sealed from outside air. However, variability of RH outside the chamber does increase variability of the measurement if the chamber is opened to outside air. This was a major issue with the initial measurements before the chamber was sealed, evacuated, and filled with dry N_2.
Lab temperature	Does not appear to influence the measurement.
Correlate different temperatures	Heating the chamber to help remove water results in a much longer time for the chamber to reach equilibrium once coolant is added.
Calibration sample #1: Aerogel Blanket (Spaceloft)	Multiple runs completed with this sample to work through various measurement parameters and protocols. More work needs to be done to quantify TC and lower error with prescribed measurement procedure.

Control Variables	Outcomes
Calibration sample #2: Microfiberglass	Excellent measurement reproducibility was obtained by NASA for calibration samples at pressures < 200 torr. This was not the case for our measurements with the Microfiberglass sample at higher pressures. NASA suggested that the difference at higher pressures was due to a change in the gas properties and the highly porous nature of the microfiber sample. This phenomena only occurred at higher pressures and created significant variability in the measurements. Our initial hypothesis is that this phenomena is related to residual water in the chamber. Our experience with fumed silica and MCI samples was similar to the Microfiberglass sample.

Subject Inventions Listing:

- "Conductive Polymers with Reduced Radiative Transport and Emissivity." *U.S. Provisional Patent Application No. 63/021,395.*
- "Crosslinking of Loose Insulating Powders." *U.S. Provisional Patent Application No. 63/021,381.*

ROI #:

- Simpson, L. J.; Engtrakul, C. Conducting Polymers to Reduce Radiative Transport and Emissivity, and to Crosslink Powders (NREL ROI-19-156).
- Simpson, L. J.; Engtrakul, C. Crosslinking of Loose Insulating Powders (NREL ROI-19-155).
- Simpson, L. J.; Engtrakul, C. Boron, Fibers, and/or Multimodal Sizes to Strengthen Crosslinked Particles (NREL ROI-20-04).